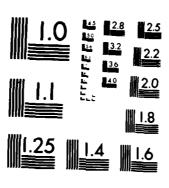
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Resonance Fluorescence of a Two-Level Atom Near a Metal Surface

by

Xi-Yi Huang, Jui-teng Lin and Thomas F. George

Prepared for Publication

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Department of Chemistry University of Rochester Rochester, New York 14627 SELECTE S
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METAL SURFACE LASER BANDWIDTH

REFLECTED FIELD PHASE-DIFFUSION MODEL POPULATION INVERSION OSCILLATORY BEHAVIOR

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Journal of Chemical Physics, in press

RESONANCE FLUORESCENCE OF A TWO-LEVEL ATOM NEAR A METAL SURFACE

Xi-Yi Huang, (a)* Jui-teng Lin(b) and Thomas F. George (a)

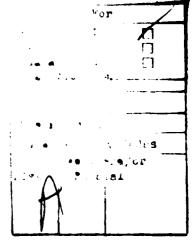
- (a) Department of Chemistry, University of Rochester Rochester, New York 14627
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Abstract

A derivation of surface-dressed optical Bloch equations, involving a treatment of surface-reflected photons and a surface plasmon resonance, is presented for a collision-damped two-level atom near or adsorbed on a metal surface. Effects of the laser bandwidth are included by means of a phase-diffusion model for the driving field. In the weak-field or large detuning limit, the population inversion and resonance fluorescence spectrum are obtained analytically. These quantities along with the surface-induced phase-decay constant of the adatom show strong oscillatory behavior as a function of the adatom-surface distance.

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I. Introduction

Recently there has been considerable interest in the interaction of electromagnetic radiation with surfaces. The experiments which have motivated this present paper are those demonstrating the high intensity of light inelasticially scattered from molecules adsorbed on metal surfaces and the surface-enhanced luminescence of an excited molecule fluorescing near or on metals and dielectric fibers. 2-4

To investigate the basic behavior of the surface-enhanced resonance excitation of a laser-driven quantum system near or adsorbed on a surface, as a first step we calculate the resonance fluorescence spectrum of a two-level atom near or adsorbed on a metal surface. In the surface-free case, i.e., in the absence of a solid surface or when the atom is very far from the surface, resonance excitation of a two-level atom by a laser field has been extensively investigated, using the powerful optical Bloch equations. There has also been interest in surface-enhanced spontaneous emission of two-level atoms near a mirror. In this paper, we provide a derivation of the surface-dressed optical Bloch equations. The following factors are taken into account:

- i) Radiative spontaneous decay and stimulated emission produced by both the driving laser field and the reflected electromagnetic field.
- ii) Collisional dephasing of the two-level atom produced by foreign atoms in the gas medium, which constitutes the half region of the interface.
- iii) The oscillatory behavior of the lifetime of the adatom due to interference between the driving field and the reflected field.

- iv) Surface-induced dephasing of the adatomic transition dipole.
- v) The interaction between the adatom and surface plasmons.
- vi) The random phase fluctuation of the laser field and its influence on the spectrum.

In Section II we derive the surface-dressed optical Bloch equations. In Section III we solve the equations in the weak-field limit to obtain the population inversion and the resonance fluorescence spectrum. In Section IV we present results for these quantities and the surface-induced phase-decay constant of the adatom. Section V is the Summary.

II. Surface-Dressed Optical Bloch Equations (SBE)

Let us consider a laser-driven two-level atom near or adsorbed on a metal surface. Although the atom has no dipole moment in its ground state, it can have a significant transition dipole connecting the ground and excited states. The reflected field provided by a metallic mirror and surface plasmon resonance can influence the dynamic behavior and scattering spectrum of the adatom.

To treat this problem we utilize a self-consistent approach. This first involves the determination of the induced transition dipole by quantum mechanics, i.e., the optical Bloch equations. The transition dipole is then used in Maxwell's equations to determine the reflected field, and the reflected field in turn is used in the quantum mechanical procedure to find the transition dipole. The resulting form of the reflected field $\hat{E}_{R}(t)$ is

$$\hat{E}_{R}(t) = \mu_{12}\hat{\sigma}_{12}(t)f(d) + \mu_{21}\hat{\sigma}_{21}(t)f^{*}(d), \qquad (1)$$

where d is the distance between the adatom and surface, μ_{ij} is the electric-dipole transition matrix element between the states $|i\rangle$ and $|j\rangle$, $\sigma_{ij}\equiv|i\rangle\langle j|$ is the adatomic transition operator, and f(d) is a distance-dependent function which will be discussed in more detail later. The SBE in operator form are then given by (assuming the equilibrium condition $\hat{W}=-1$)

$$\frac{\partial}{\partial t} \hat{\sigma}_{21}(t) = (i\omega_{21} - \gamma_2)\hat{\sigma}_{21}(t) + i\frac{\mu_{21}}{4!} \hat{W}\{\hat{E}(t) + [f(d)\omega_{12}\hat{\sigma}_{12}(t) + f^*(d)\omega_{21}\hat{\sigma}_{21}(t)]\}$$
(2)

$$\frac{\partial}{\partial t} \hat{W}(t) = -\gamma [1 + \hat{W}(t)] + 2i \frac{\mu_{21}}{A} \hat{\sigma}_{21} \{\hat{E}(t) + [f(d)\mu_{12}\hat{\sigma}_{12}(t)] + f^*(d)\mu_{21}\hat{\sigma}_{21}(t)]\} \sim 2i \frac{\mu_{12}}{A} \hat{\sigma}_{12} \{\hat{E}(t) + [f(d)\mu_{12}\hat{\sigma}_{12}(t)] + f^*(d)\mu_{21}\hat{\sigma}_{21}(t)]\}$$
(3)

$$\frac{\partial}{\partial t} \hat{\sigma}_{12}(t) = \frac{\partial}{\partial t} \hat{\sigma}_{21}^{\dagger}(t), \tag{4}$$

where ω_{21} is the adatomic transition frequency, $\hat{E}(t)$ is the random phase-fluctuating electric field strength operator, γ_1 is the population relaxation constant, γ_2 is the phase relaxation constant, and $\hat{W}(t) \equiv \hat{\sigma}_{22}(t) - \hat{\sigma}_{11}(t)$ is the population inversion of the adatom. Collisions of the adatom with other atoms in the gas medium are accounted for in the impact limit by assuming $\gamma_1 \neq 2\gamma_2$.

The quantum equations of motion for \hat{W} , $\hat{\sigma}_{12}$ and $\hat{\sigma}_{21}$ are most useful in the rotating-wave approximation (RWA). By defining

$$\hat{S}_{12}(t) \equiv \hat{\sigma}_{12}(t)e^{i\omega_L t} \tag{5}$$

$$\hat{S}_{21}(t) = \hat{\sigma}_{21}(t)e^{-i\omega_L t},$$
 (6)

where ω_L is the laser frequency, we can rewrite Eq. (2.2) within the RWA as

$$\frac{d}{dt} \begin{pmatrix} \hat{S}_{21}(t) \\ \hat{W}(t) \\ \hat{S}_{12}(t) \end{pmatrix} = \begin{pmatrix} -\tilde{\gamma}_{2} + i\Delta & i\Omega^{-}(t)/2 & 0 \\ i\Omega^{+}(t) & -\gamma_{1} & -i\Omega^{-}(t) \\ 0 & -i\Omega^{+}(t)/2 & -\tilde{\gamma}_{2} - i\Delta \end{pmatrix} \begin{pmatrix} \hat{S}_{21}(t) \\ \hat{W}(t) \\ \hat{S}_{12}(t) \end{pmatrix}$$

$$-\gamma_{1} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}. \tag{7}$$

 $\Omega^{\pm}(t) \equiv \Omega \exp\left[\mp i\phi(t)\right]$ is the time-dependent Rabi frequency, where $\Omega \equiv \frac{2}{\pi}|u_{21}|E_0(t)$ and E(t) is written as an expectation value in a coherent state of the laser field in terms of the phase factor $\phi(t)$ as $E(t) = E_0(t)\exp\left[-i\omega_L t + i\phi(t)\right] + c.c.$; $\Delta \equiv \omega_{21} - \omega_L$ is the detuning; the surface-induced phase-decay constant is $\gamma_\Delta \equiv \frac{2}{\pi} \operatorname{Im}(f)|u_{12}|^2$; and $\tilde{\gamma}_2 = \gamma_2 + \gamma_\Delta$.

To calculate γ_{A} , we must know the reflected field [Eq. (1)] or the complex function f(d), which can be determined by the Sommerfeld-Hertz vector procedure. For the case of a laser-excited atom emitting near a metallic half space, the imaginary part of f(d) has the following form:

where $\zeta=1$ and $\eta\equiv\frac{1}{D^3}+\frac{1}{D}$ for the case of the induced dipole oriented parallel to the surface, $\zeta=2$ and $\eta\equiv\frac{1}{D^3}$ for the perpendicular case, ε_1 is the dielectric constant for the gas medium, $k_1=\omega\sqrt{\varepsilon_1}/c$ is the wave number, ω is the emission frequency, c is the speed of light, and $D=2k_1d$ is the reduced distance which is dimensionless. The Drude model 10 has been used to determine the dielectric constant of the metal medium, i.e.,

$$\varepsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + 16)}, \qquad (9)$$

where δ is the inverse of the relaxation time and ω_p is the plasma frequency. We note that Im(f) has a resonance at $\omega_{\Delta p} = \omega_p (1+\varepsilon_1)^{-1/2}$, which is the surface plasmon frequency of the interface, so that the reflected field given by Eq. (1) involves resonance energy transfer between the adatom and the excited surface plasmon.

Eq. (8) leads to a surface-induced phase-decay constant (in the unit of Einstein's spontaneous decay constant A = $\frac{4\omega_{21}^3}{3hc} |\mu_{21}|^2$) of the following form:

$$\gamma_{\delta} = \zeta a_0 [a_1(\eta \sin D - \frac{\cos D}{D^2}) + a_2(\eta \cos D + \frac{\sin D}{D^2})],$$
 (10)

where

$$a_0 = \frac{3}{8} \frac{1}{(1-\beta^2)^2 + (\alpha/\omega_{AD})^2}$$
 (11)

$$a_1 = (2-\beta^2)^2 + (2\alpha/\omega_{AD})^2 - \beta^4$$
 (12)

$$a_2 = (2\beta)^2 \alpha/\omega_{\delta p}, \tag{13}$$

 $\beta \equiv \omega_L/\omega_{\Delta p}$, $\alpha \equiv \delta/\beta$, ζ and η are the same as in Eq. (8) for the parallel and perpendicular cases, and $\varepsilon_1 = 1$ has been assumed so that $\omega_{\Delta p} = \omega_p/\sqrt{2}$. The above expression for γ_{Δ} can be further simplified by assuming perfect reflection, i.e., $R^{\perp} = R^{\parallel l} = -1$, where $R^{\parallel l}$ is the reflection coefficient for an incident ray polarized parallel to the plane of incidence (p-polarized) and R^{\perp} is the reflection coefficient for perpendicular polarization (a-polarized). Then

$$\gamma_{\Delta} = \frac{3}{2} \zeta(n \sin D - \frac{\cos D}{D^2}). \tag{14}$$

III. Resonance Fluroescence Spectrum

In this section we consider the weak field or large detuning limit, where W(t) $\equiv <<\hat{W}(t)>> = -1$. We also use the phase-diffusion model 11,12 for the laser field in order to include the effects of the laser bandwidth γ_L :

$$<<\Omega^{-}(t_{1})\Omega^{+}(t_{2})>> = \Omega^{2}e^{-\gamma_{L}|t_{2}-t_{1}|}.$$
 (15)

The double bracket signifies two averages: one is over the stochastic ensemble, and the other is a standard quantum mechanical average. Eq. (15) applies to a partially-coherent laser field, which is the realistic situation. Given that the atom near the metal remains more or less in in its ground state, we can linearize Eq. (7) to obtain

$$\frac{d}{dt} \hat{S}_{21}(t) = -(\gamma_2 + \gamma_A - i\Delta) \hat{S}_{21}(t) - \frac{i}{2} \Omega^{-}(t).$$
 (16)

To determine the population inversion, let us take the laser field to be turned on at t=0 with a constant amplitude for $t\geq 0$. We then obtain the analytical form

$$W(t) = -1 + \Omega^{2} \{ \frac{\tilde{\gamma}_{2}^{+\gamma_{L}}}{\gamma_{1} [(\tilde{\gamma}_{2}^{+\gamma_{L}})^{2} + \Delta^{2}]} + \frac{\gamma_{1}^{-\tilde{\gamma}_{2}^{-\gamma_{L}}}}{\gamma_{1} [(\gamma_{1}^{-\tilde{\gamma}_{2}^{-\gamma_{L}}})^{2} + \Delta^{2}]} e^{-\gamma_{1}t}$$

$$- \frac{[(\tilde{\gamma}_{2}^{+\gamma_{L}})(\gamma_{1}^{-\tilde{\gamma}_{2}^{-\gamma_{L}}}) + \Delta^{2}] \cos(\Delta t) + \Delta(2\tilde{\gamma}_{2}^{-2\gamma_{L}^{-\gamma_{1}}}) \sin(\Delta t)}{[(\tilde{\gamma}_{2}^{+\gamma_{L}})^{2} + \Delta^{2}][(\gamma_{1}^{-\tilde{\gamma}_{2}^{-\gamma_{L}}})^{2} + \Delta^{2}]}$$

$$= -(\tilde{\gamma}_{2}^{-\gamma_{L$$

To obtain the power spectrum of the scattered light, we must find the dipole-dipole correlation function $<<\hat{S}_{21}(t_2)\hat{S}_{12}(t_1)>>$. For $t_1,t_2>> \gamma_1^{-1},\gamma_2^{-1}$ this takes the form $(t_2 \ge t_1)$

$$<<\hat{S}_{21}(t_2)\hat{S}_{12}(t_1)>> = \frac{\Omega}{4} \frac{1}{(\hat{\gamma}_2 + \gamma_L) + i\Delta}$$

$$\times \frac{2(\hat{\gamma}_2 + \gamma_L)(\hat{\gamma}_2 - \gamma_L - i\Delta) - \gamma_1[(\hat{\gamma}_2 + \gamma_L) - i\Delta]}{\gamma_1(\hat{\gamma}_2 + \gamma_L - i\Delta)(\hat{\gamma}_2 - \gamma_L - i\Delta)} e^{-(\hat{\gamma}_2 - i\Delta)(t_2 - t_1)}$$

$$(continued)$$

(continued)

$$+\frac{\Omega^2}{4}\frac{e^{-\gamma_L(t_2-t_1)}}{(\tilde{\gamma}_2+\gamma_L+1\Delta)(\tilde{\gamma}_2-\gamma_L-1\Delta)}.$$
 (18)

The corresponding power spectrum for the emitted frequency ω is given by the Fourier transform of the above equation:

$$S(\omega) = \frac{\Omega^{2}}{2} \frac{1}{(\tilde{\gamma}_{2} + \gamma_{L})^{2} + \Delta^{2}} \left\{ \frac{1}{(\tilde{\gamma}_{2} - \gamma_{L})^{2} + \Delta^{2}} \left[\frac{\gamma_{L}(\tilde{\gamma}_{2}^{2} - \gamma_{L}^{2} + \Delta^{2}) + 2\gamma_{L}\Delta(\omega - \omega_{L})}{\gamma_{L}^{2} + (\omega - \omega_{L})^{2}} \right] \right\}$$

$$-\frac{\tilde{\gamma}_{2}(\tilde{\gamma}_{2}^{2}-\gamma_{L}^{2}+\Delta^{2})+2\gamma_{L}\Delta(\omega-\omega_{21})}{\tilde{\gamma}_{2}^{2}+(\omega-\omega_{21})^{2}}]+\frac{2(\tilde{\gamma}_{2}+\gamma_{L})\tilde{\gamma}_{2}}{\gamma_{1}[\tilde{\gamma}_{2}^{2}+(\omega-\omega_{21})^{2}]}$$
(19)

The fluorescence spectrum of Eq. (19) generally exhibits two peaks for a surface-dressed two-level atom in a weak, partially-coherent laser field. One peak is centered at $\omega = \omega_1$, which corresponds to elastic or Rayleigh scattering, and the other near $\omega = \omega_{21}$ corresponds to inelastic scattering or fluorescence. In the surface-free case for a collisionless atom in a fully-coherent laser field $(\gamma_1 = 2\gamma_2 = A, \gamma_1 = 0)$, the above spectrum becomes a single peak,

$$S(\omega) = \frac{\pi\Omega^2/2}{(A/2)^2 + \Delta^2} \delta(\omega - \omega_L), \qquad (20)$$

which is the standard result of Heitler. 13 In general, however, the adatom suffers collisions with foreign atoms in the gas medium, so that $\gamma \neq 2\gamma_2$, and there are nonzero values for the surface-induced phase-decay constant γ_{Δ} and the laser bandwidth γ_{L} . This is then responsible for the second Lorentzian peak occurring near the transition frequency ω_{21} .

IV. Results

Fig. 1 shows the time evolution of the population inversion W(t)[Eq. (17)] for an atom near a metal surface for two different adatomsurface plasmon resonance conditions, $\beta \equiv \omega_{\rm L}/\omega_{\rm Ap} = 0.5$ and $\beta = 0.9$. We have used the value of 3.5 x 10^{-3} for the ratio δ/ω_{AD} , which corresponds to a silver surface. Each curve approaches a stationarystate value, assuming that the duration of the laser pulse is much longer than the relaxation time of the adatom (characterized by γ_1^{-1} and $\tilde{\gamma}_2^{-1}$). The reason the values of W for the off-resonance case (β = 0.5) are less than those for the near-resonance case (β = 0.9) is that the levels of the adatom in the latter case are strongly broadened by the resonant transfer of energy between the adatom and surface plasmon, so that the population of the upper level increases. The oscillations increase and the damping due to the reflected field disappears as the adatom moves further from the surface (going from curve 1 to 3). The strong oscillations in the nearly surface-free case (curve 3) are caused by beating between the driving laser field and the "adatomic oscillator".

Fig. 2 displays the resonance fluorescence spectrum [Eq. (19)], with the Rayleigh and fluorescence peaks. The former peak in our

model is just determined by the laser bandwidth γ_L . The latter peak is strongly dependent on the adatom-surface distance; as the distance decreases, the upper adatomic level broadens and hence the fluroescence intensity increases.

In Fig. 3 we plot W(t) for the case of a perfectly reflective metal surface, $R^{\perp}=R^{\parallel}=-1$ [see Eq. (14)], for several values of the laser bandwidth and adatom-surface distance. The oscillations increase as the adatom moves further from the surface and decrease as the laser bandwidth increases [going from (a) to (c)]. A larger bandwidth leads to more damping of the adatomic oscillator [see Eq. (17)] and hence an increase in the population inversion. It is interesting to note that W is more sensitive to the adatom-surface distance for the case of the transition dipole oriented parallel to the surface than for the perpendicular case. We see that the positions of the dashed curves 2 and 3 are interchanged, indicating that the power spectrum oscillates as a function of D. As seen by the form of Eq. (8), we would also see such oscillations for the population inversion and power spectrum in Figs. 1 and 2 if we were to consider a wider range of values of D.

Fig. 4 displays the surface-induced phase-decay constant γ_{A} as a function of the adatom-surface distance for a perfectly reflective surface. The oscillations are due to the interference between the reflected field and the driving field. This gives rise to oscillations in the lifetime of the adatomic oscillator, while the small negative value of γ_{A} in some regions of D tends to increase the lifetime.

Fig. 5 shows the power spectrum for several values of the laser bandwidth γ_L . When γ_L is very small compared to the phase-decay constant γ_2 [Fig. 5(a)],

the power is concentrated largely in the Rayleigh peak. Here the population of the upper adatomic level, and hence the power of the fluorescence, is determined mainly by the broadening of that level due to the surface, so that the power increases as D decreases. The situation is changed when γ_L is larger than γ_2 , in which case the power of the Rayleigh component transfers to the fluorescence peak [Fig. 5(b) and (c)]. Although a decrease in D leads to a broadening of the adatomic level, now the total power in the fluorescence peak is approximately unchanged, whereby a curve for smaller D has a larger width but a smaller peak height. A more detailed discussion on the relation between fluorescence and laser bandwidth in general will be published later.

It is interesting to note that Weitz et all recently published measurements and a theoretical model on a hierarchy of enhancement ratios for normal Raman scattering, resonance Raman scattering and fluorescence from molecules adsorbed on a silver surface: 14 The results from our two-level adatom model for surface-enhanced fluorescence are in good agreement with their measured enhancement ratio of 10^{-1} to 10 for fluorescence.

V. <u>Summary</u>

A simple model has been developed to describe the dynamic behavior of a two-level adatom at a metal surface. Surface-dressed optical Bloch equations (SBE), which account for surface-reflected photons and adatom-surface plasmon coupling, have been derived. Collisions with foreign gas atoms and effects of the laser bandwidth have been included. The SBE have been used to evaluate the power spectrum of the scattered light, the population inversion and the surface-induced phase-decay constant as functions of the adatom-surface distance and adatom-surface plasmon resonance parameter β . The displayed properties of the laser-adatom-surface system should be useful in understanding basic processes occurring in surface resonance spectroscopy.

Acknowledgments

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AFOSR 82-0046 and the U.S. Army Research Office. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

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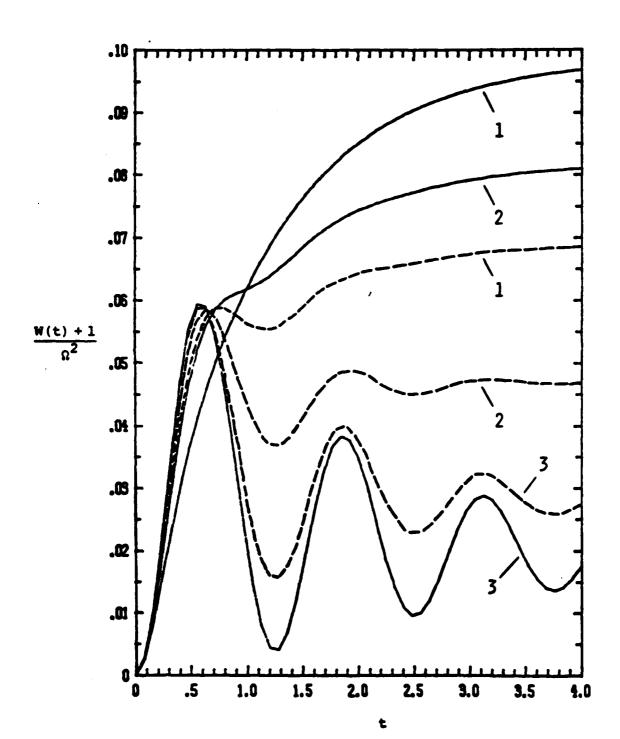
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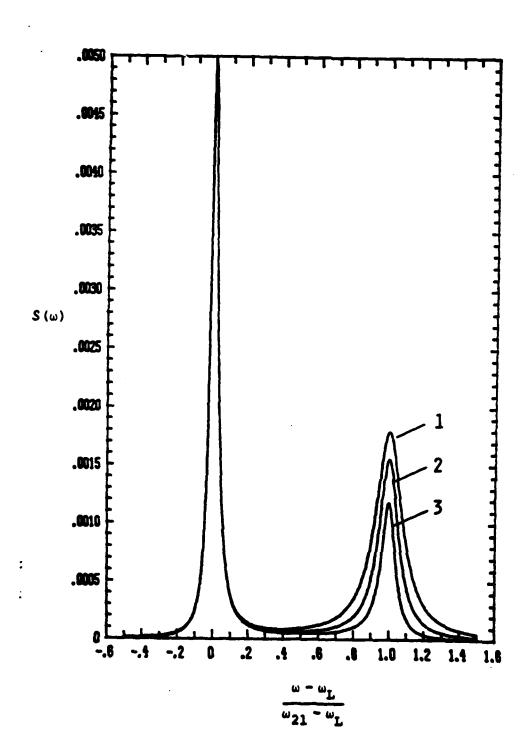
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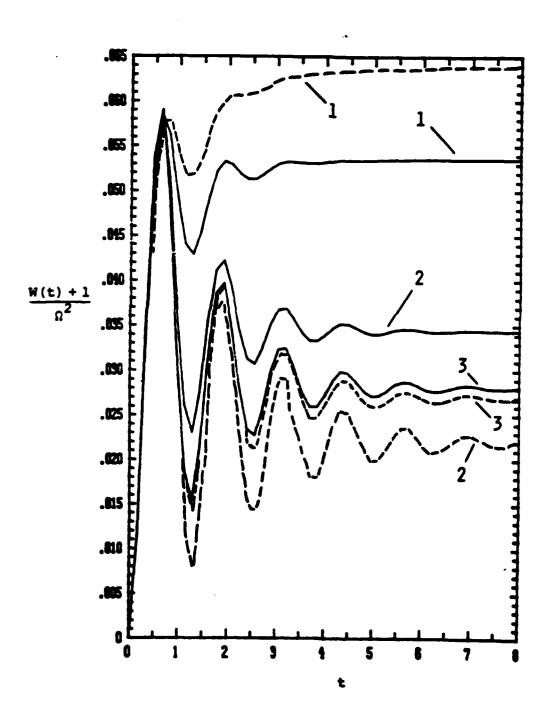
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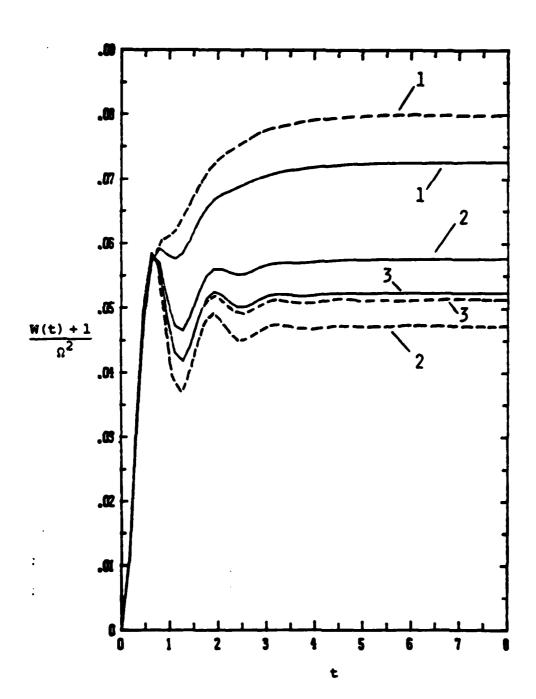
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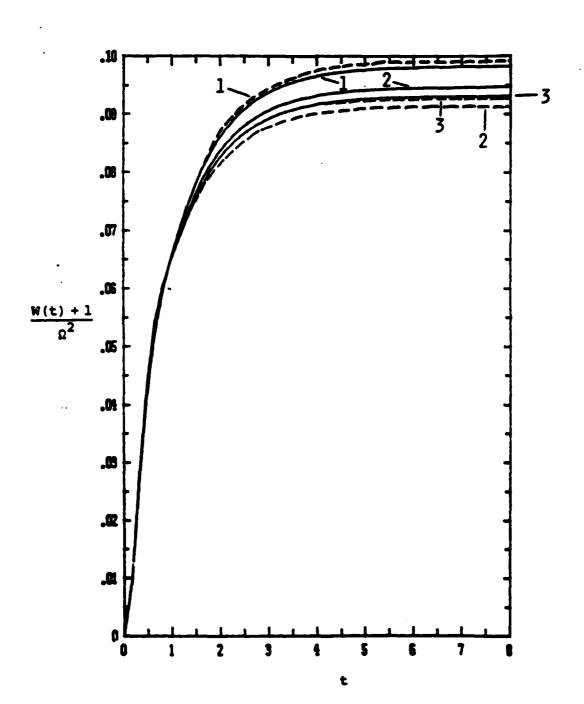
- 1. Time evolution of the population inversion in the weak field or large detuning limit, with $(\gamma_L, \Omega, \Delta) = (0.3, 0.05, 5)$ in the unit A for $\beta = 0.9$ (solid curves) and $\beta = 0.5$ (dashed curves). Curves 1, 2 and 3 correspond to the values of the reduced distance $D = 2k_1d$ of 1, 3 and 5, respectively. The horizontal axis corresponds to time in the unit A^{-1} . The quantity $[W(t)+1]/\Omega^2$ is shown along the vertical axis.
- 2. Fluorescence power spectrum of scattered light with $(\gamma_L, \Omega, \Delta) = (0.3, 0.05, 5)$ in the unit A and $\beta = 0.9$ for the induced transition dipole oriented perpendicular to the surface. The units along the vertical axis are arbitrary. Curves 1, 2 and 3 correspond to D = 1, 3 and 5, respectively.
- 3. Time evolution of the population inversion W(t) of an adatom at a perfectly reflective metal surface, with $\Omega=0.05$, $\Delta=5$, (a) $\gamma_L=0.3$, (b) $\gamma_L=1$, and (c) $\gamma_L=3$ (in the unit A). The solid curves are for the induced transition dipole oriented perpendicular to the surface, while the dashed curves are for the parallel case, and the labels 1, 2 and 3 correspond to D = 2, 4 and 6, respectively.
- 4. Surface-induced phase-decay constant γ_{δ} (in the unit A) as a function of the reduced adatom-surface distance D = $2k_1d$ for a perfectly reflective metal surface. The solid curve is for the induced transition dipole oriented perpendicular to the surface, while the dashed curve is for the parallel case.
- 5. Power spectrum of scattered light for a perfectly reflective metal surface, with $\Omega=0.05$, $\Delta=5$, (a) $\gamma_L=0.3$, (b) $\gamma_L=1$ and (c) $\gamma_L=3$ (in the unit A). The induced transition dipole is oriented perpendicular to the surface. The units along the vertical axis are arbitrary. Curves 1, 2 and 3 correspond to D = 2, 4 and 6, respectively.

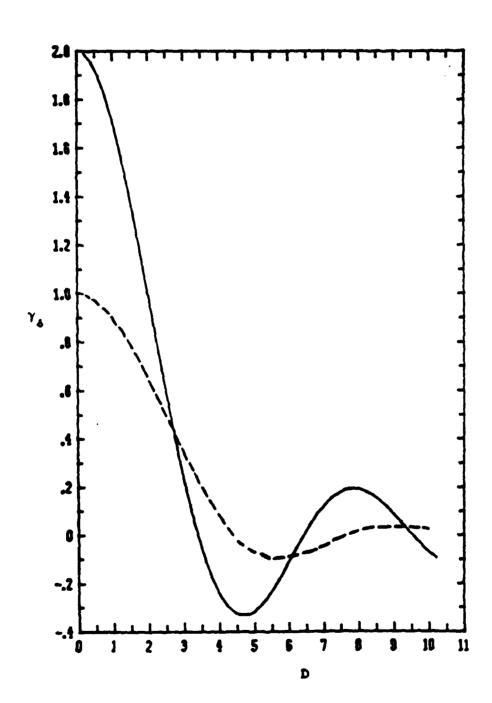


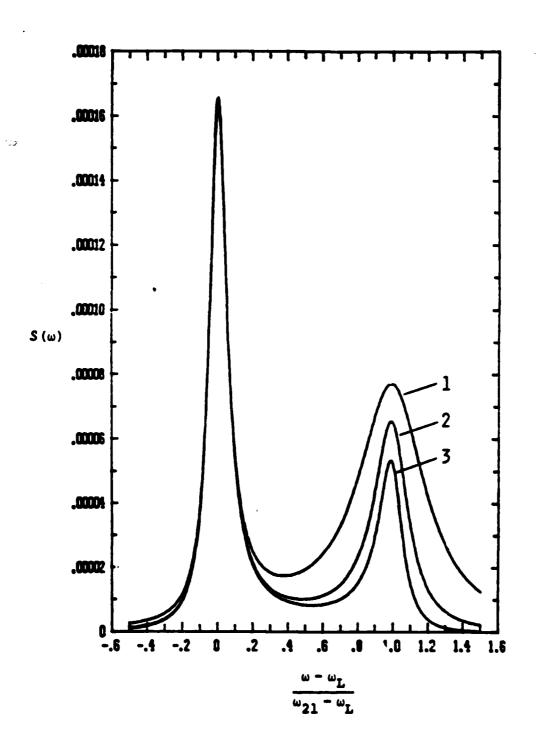


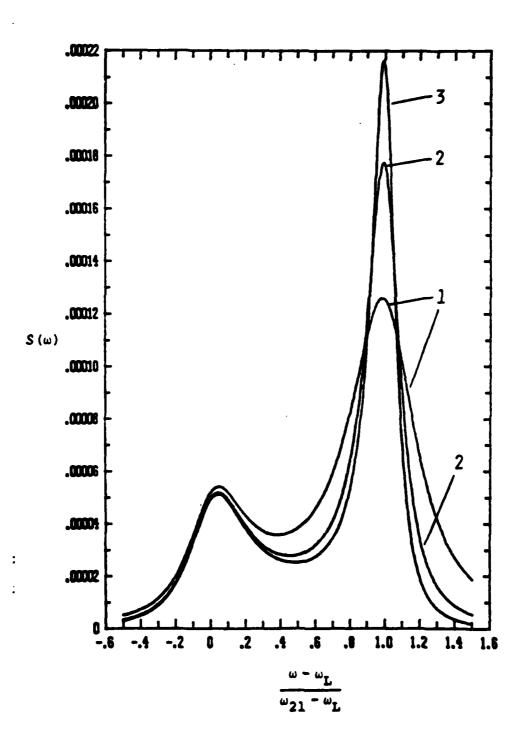


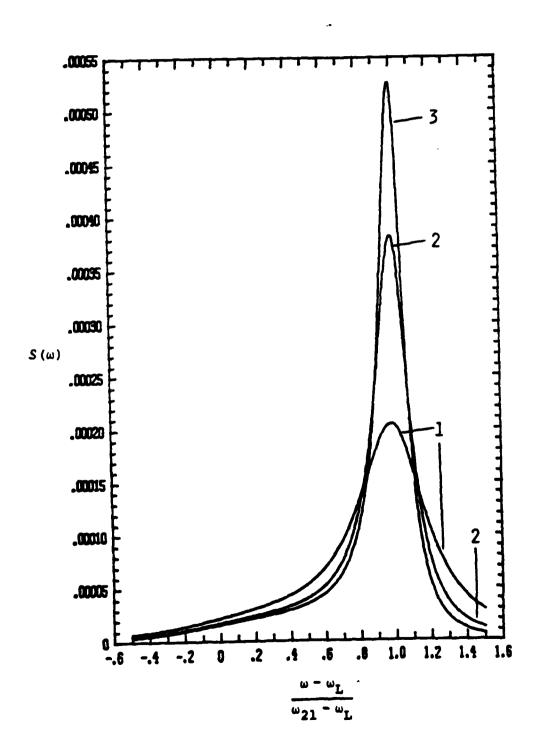












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